



PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in Sorel Cement

We, H. H. ROBERTSON COMPANY, a corporation organized under the laws of the Commonwealth of Pennsylvania, of Farmers Bank Building, Pittsburgh, 5 County of Allegheny, Commonwealth of Pennsylvania, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to a cement and more particularly to an oxychloride cement.

15 The object of the invention is to improve the copper bearing oxychloride cements forming the subject matter of the specification of our British Patent No. 465,240, particularly with respect to the 20 form in which copper is incorporated in the oxychloride cement whereby there is imparted to the cement improved water resistance and stability as well as other superior characteristics, as will be herein- 25 after described.

With this general object in view, and such others as may hereinafter appear, the invention consists in the improved oxychloride cement and its preparation as 30 hereinafter described.

As set forth in the specification above referred to, the water resistance, stability, and general commercial utility of Sorel, i.e. oxychloride cements, and particularly 35 of magnesium oxychloride cements, have been greatly improved and increased by the incorporation into the oxychloride cements of minor proportions of finely divided metallic copper or finely divided 40 cuprous oxide, whose particles may for example have an average diameter of eight microns. Prior to the invention of the superior copper bearing oxychloride cements forming the subject matter of the 45 patent above referred to, it was generally recognized that magnesia cements were disqualified from many industrial and commercial uses because of the extent to which their cementing constituent dis-

solved in water. The incorporation of 50 copper either in the form of finely divided metallic copper or in the form of cuprous oxide in a minor proportion, as for example from 3 to 10%, proved to be 55 substantially beneficial to the cement and to increase its water resistance and strength.

When the minor proportion of finely divided metallic copper or cuprous oxide is added to the magnesia cement and the 60 latter is permitted to harden, the cement gradually assumes a characteristic bluish-green color during the hardening process and the increased strength and water 65 resistance of the cement develops as this bluish-green characteristic color is developed. While the exact mechanism of the reactions which actually take place between the finely divided copper or 70 cuprous oxide and the constituents of the magnesia cement during the hardening process are not well understood, nevertheless experience has demonstrated that the cements are improved when the metallic 75 copper and cuprous oxide is incorporated in a finely divided condition as above mentioned.

The reactivity of the metallic copper and cuprous oxide in this extremely finely 80 divided condition facilitates the reaction thereof with the ingredients of the cement to form insoluble copper compounds. The reaction product occupies more space than the original copper particle or original 85 cuprous oxide particle, and as it forms it apparently swells effectively filling capillaries and interstices in the cement with the insoluble copper compounds. It will be apparent, therefore, that the rate 90 of corrosion or rate of the reaction of the copper or cuprous oxide with the cement plays an important part in improving the water resistance and strength of the oxychloride cement.

The commercial forms of finely divided 95 metallic copper which have been heretofore available have however lacked stability in the air and all tend to oxidize

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to the black or cupric state. This is particularly true when humid atmospheric conditions are encountered.

According to the present invention, in order to produce a cement in which the finely divided copper, that is added to the oxychloride cement, contains a minimum amount of cupric oxide so as to be in a condition to react readily with the other constituents of a Sorel cement particularly magnesium oxychloride cement, there is employed a mixture of finely divided copper, the particles of which have protective cuprous oxide films thereon, and a substantial proportion of particles of cuprous oxide, the resultant cupreous powder having the major portion of its particles of a size of a few microns, e.g. two, the said cupreous powder being present in an amount substantially less than the amount of the cement.

Such mixture consisting mainly of copper particles coated with a film of cuprous oxide and particles of cuprous oxide is advantageously produced by precipitating a solution of copper, e.g. by a scrap iron or electrolysis, the precipitate being known commercially as "cement copper" or "copper precipitate," and afterwards drying such precipitate rapidly and reducing it in an impaction mill to an extremely finely divided condition having a particle size of e.g. two microns. By this means there is produced a dry cupreous powder comprising essentially metallic copper particles having protective cuprous oxide films thereon and a substantial proportion of cuprous oxide, this cupreous powder being present in the magnesium oxychloride cement in an amount substantially less than the amount of the cement. This cupreous product is characterized by a high degree of stability in the air and at the same time the copper is present therein in a form which has been found to be not only stable in the air but highly reactive when exposed to conditions such as are present in a magnesium or other oxychloride cement during the hardening thereof.

"Cement copper" or "copper precipitate" as produced at the mines or refineries comprises a brownish red sludge, wherein the copper is present in the form of a peculiar crystalline form of copper particle dendritic in nature and capable of being easily crushed when subjected to impact as by passing through one of several types of hammer-mills, jet pulverizers and ball mills. The commercial "cement copper" and "precipitated copper" sludge in the condition obtainable from the refineries contains impurities including compounds of iron,

aluminium and silica and which for the purposes of the present invention may be regarded merely as inert diluents. Along with such impurities commercial cement copper contains cuprous oxide in varying amounts from a small amount up to 40% and in some instances more, depending upon the method employed in precipitating the material at the mines. For example, cement copper obtained from Western mines has averaged about 18% cuprous oxide, whereas a cement copper obtained from Eastern sources averaged in the neighborhood of 40 to 42% of cuprous oxide.

When such copper sludge was air dried according to prior practice the product blackened, resulting in a cupreous product having a high cupric oxide content and this product could not be used for the production of the improved oxychloride cements forming the subject matter of the patent above referred to. Freshly precipitated copper has also been dried in a reducing atmosphere to produce a bright oxide-free cupreous powder, but this powder is relatively unstable in the air, tends to blacken quickly, and has proved to be unsatisfactory in commercial practice when the attempt has been made to use it in the production of such cements.

In order to produce the present stable in the air cupreous pigment the cement copper or precipitated copper sludge preferably in its unrefined condition and in any event without being subjected to chemical treatment which would effect the removal of its cuprous oxide content, is shipped from the refinery in a damp state and in such a manner as to minimize further oxidation of the copper and so that the cement copper or precipitated copper when received is substantially free from cupric oxide. This may be accomplished in practice by shipping the damp material in a tight container or by shipping it in a bulk mass in which the moisture content is so high that all interstices between the particles are filled with water and the air is consequently excluded. Experience has shown that a minimum amount of water of 22% will accomplish this result. The damp and incompletely oxidized cement copper or copper precipitate sludge as thus received, is subjected to further processing as follows: The wet sludge is subjected to treatment to remove the water therefrom as rapidly as possible. Heretofore commercial cement copper or precipitated coppers have been regarded as unstable; since damp copper oxidizes with great rapidity when exposed to the air, especially when heated and oftentimes at a rate approaching spontaneous combustion.

Accordingly the removal of moisture from the sludge is effected as rapidly as possible in order to shorten the interval during which the drying copper particles are exposed to severe oxidizing conditions. This may be accomplished in any of several types of drying equipment in which moisture is rapidly evaporated and swept away from thin layers of the powder at temperatures not greatly in excess of the boiling point of water. For example direct or indirect fired rotary driers; and heated surfaces over which thin layers of the powder are moved; conveyors that move the powder in thin layers while it is heated by radiation or by hot gases have been found satisfactory.

Satisfactory results have also been obtained by subjecting the material to a combined drying and crushing operation providing the moisture content is not excessively high, employing hot products of combustion, e.g. clean combustion gases from coal fired furnaces, as the circulating medium in a mill of the type of the "Raymond Imp" mill, i.e. a mill of the type in which provision is made for grinding material to a state of minute subdivision and for retaining and collecting such material, additional air being introduced into the mill and circulated during the operation.

In practice it has been found to be desirable to accomplish the drying in two stages, one immediately following the other. In the first stage the damp sludge is given a preliminary drying down to approximately 10 per cent. of water by a drying equipment in which moisture is rapidly evaporated and swept away from thin layers of the sludge at temperatures not greatly in excess of the boiling point of water. In this drying the formation of dust is avoided by discharging the material from the drying equipment when the moisture content above mentioned (10%) is reached, which is above the point where dust is produced.

The sludge partially dried in the first stage is immediately transferred to a mill where the second stage in the drying process takes place simultaneously with its reduction to a fine powder that has a particle size of a few microns, e.g. two. In this stage, the partially dried powder is given its final drying to remove the moisture as completely as possible e.g. to 0.2 to 0.4%, as even one or two per cent. of moisture causes oxidation of the copper to the cupric state, resulting in a blackened and commercially unsatisfactory product.

On entering this second stage of the drying process, the partially dried sludge comprises friable copper dendrites and a

varying but substantial content of cuprous oxide and containing very little, if any, cupric oxide. The final drying and pulverization is accomplished by passing the material through an impaction mill, such as a hammermill or a jet pulverizer, through which air is preferably circulated along with hot products of combustion, e.g. clean combustion gases from coal fired furnaces. The pulverizing action upon the cement copper not only crushes it to extreme fineness, wherein the particle size is reduced to a few, e.g. two microns but also produces the most unexpected result of imparting to the material the ability to resist further oxidation when exposed to atmospheric conditions. In order to discover the underlying reasons for the high reactivity of the present finely divided cupreous material and its remarkable air stability, extended research was carried on including chemical analysis of the cupreous powder product as above described. The results of such analyses disclosed that the cuprous oxide content was not appreciably increased during the passage of the material through the mill and further that additional passes through the mill did not effect any further oxidation of the copper to cuprous oxide. X-ray studies and also inspection of polished surfaces cut through the particles and viewed, when illuminated by reflected light with a magnification of 1000 diameters demonstrated that the cupreous powder comprised copper particles having thin surface films of cuprous oxide thereon, which appear to serve as protective films therefor. Among the film covered copper particle occasional small grains of oxidized copper (Cu_2O) were disclosed which obviously afforded no protection for the copper particles. Examination of cupreous products produced from cement copper from different sources and which contained widely varying amounts of cuprous oxide, as for example variations from 18 to 42% cuprous oxide, demonstrated that the surface film was of substantially the same thickness irrespective of the original cuprous oxide content. The original granular form of the cuprous oxide in the unprocessed cement copper indicates its unprotective nature and explains the reason why the unprocessed cement copper readily oxidizes to cupric oxide.

The research has indicated that the novel air stable and highly reactive cupreous powder can be produced from "cement copper" or precipitated copper having a widely varying cuprous oxide content, and the lower limit of cuprous oxide content required may be stated as

being sufficient to be discernible by metallographic methods and to be identified by X-ray diffraction. When at least such an amount of cuprous oxide is present it has been found that the present process results in the production of a cupreous powder wherein the fine copper particles are coated with a thin protective film of cuprous oxide.

10 In explanation of the production of the air stable and highly reactive cupreous powder as deduced from the foregoing evidence, it will be observed that, as above stated, the unrefined cement copper, constituting the raw material which is fed to the mill, contains metallic copper particles of varying sizes in the form of friable copper dendrites and that the cuprous oxide, which may vary widely in amount as above set forth, exists in the form of solid masses or grains of varying size and which are distributed throughout the cement copper. Presumably some cuprous oxide exists on the surface of the copper particles but probably in the form of a loosely adhering scale or excrescence and not in the form of continuous film covering the copper particles. When this cement copper is subjected to the hammering action of the mill, these friable particles are broken apart and the operation is continued until the average particle diameter of the ground or crushed product is a few microns, e.g. two, since in commercial practice a fineness of the order of two microns is easily obtained. The new metallic surfaces produced by the crushing and sub-division of the particles in the mill are produced at a time when the particle is hot as a result of the impact and these surfaces are swept by an atmosphere that is at least somewhat oxidizing in nature. As a result, it is believed that a cuprous oxide film is formed on the surfaces of the individual particle and this fact is borne out by metallographic studies. Furthermore, experience justifies the belief that the cuprous oxide film produced under these conditions is continuous and serves to protect the metallic copper particles from further oxidation. For example, it is known that high temperature films of oxide on iron are more protective against further oxidation than low temperature films and furthermore that films put on by shot peening are quite resistant to further oxidation. Presumably this peening does several things—it heats the surface momentarily due to the impact and it also does some work on the film produced, probably spreading it around, compacting it and closing up the discontinuities. The action that the cupreous particles receive can be pictured as very similar to this peening for the hammermill or jet pulverizer (Micronizer) accomplish much of their result by causing particles to strike each other. Thus the particlespeen each other, producing on each other a film that is continuous and serves as a barrier to further oxidation. This protective film is very thin, as shown by the metallographs, but there are many examples of extremely thin protective films on metal surfaces, e.g. aluminium. Here, then, is an explanation of the fact that while the copper powder is remarkably stable in air, it is highly reactive in certain solutions. In these solutions the thin protective coating is removed and an enormous metallic surface is exposed. The solution rate of this exposed particle may be accelerated by the fact that metallic copper and cuprous oxide lie in close proximity and thus contribute to galvanic corrosion by creating a large number of small couples.

In accordance with the present invention the superior cupreous powder produced as above described is used with advantage instead of the metallic copper or the cuprous oxide in producing an improved cement in accordance with the teachings of the patent above referred to. Satisfactory results have been secured utilizing varying amounts of the cupreous powder and preferably from 3 to 10% by weight and this is incorporated into the cement in the form of a finely divided powder, and when such a cement is used it will be observed that during the hardening process the bluish-green characteristic color develops much more rapidly as a result of the more rapid solution of the copper and of the formation of soluble copper salts and of their reaction with the cement. This increased rate of reaction is proportional to the leach rate of the copper in the salt solutions of the cement and experience has demonstrated that the improved cupreous powder produced as above described possesses a much higher leach rate than either pure metallic copper or cuprous oxide, and as a result its reaction with the other ingredients proceeds much more rapidly and the resulting product possesses more stability, strength and water resistance than the cementitious products produced in accordance with the patent above referred to, so that the present cement is regarded as a distinct improvement thereover. Undoubtedly the presence of the cuprous oxide film and the cuprous oxide content in immediate proximity to the copper particles sets up extensive galvanic corrosion because of the vast number of small cuprous oxide-copper couples

which are formed.

Magnesium oxychloride cements are usually supplied to the user in the form of a mixture or aggregate of the dry ingredients and this dry mix is gaged at the time of use with a solution of magnesium chloride. Occasionally magnesium chloride in dry form is included in the dry mix so that it is necessary only to add water when gaging the mix. As used throughout the claims, the term "dry mixture of magnesia and aggregate" is intended to define the dry ingredients of the magnesium oxychloride cement in a condition ready to be gaged either by a solution of magnesium chloride or by water.

The percentage proportions given throughout the Specification are by weight.

Having now particularly described and ascertained the nature of the said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A cementitious material possessing superior water resistance and strength comprising a cement of the soral type, e.g. a magnesium oxychloride cement, containing a finely divided cupreous powder, the major portion of whose particles are of a size of the order of a few microns, e.g. two, said cupreous powder comprising essentially metallic copper particles having protective cuprous oxide films thereon and a substantial proportion of cuprous oxide, said cupreous powder being present in an amount substantially less than the amount of the cement.

2. An air stable cementitious material capable of being stored without deterioration for long periods of time consisting of a dry mixture of magnesia and aggregate adapted when gaged and set to produce a magnesium oxychloride cement having superior water resistance and strength, said dry mix containing a finely divided cupreous powder, the major portion of whose particles are of a size of the order of a few microns, e.g. two, said cupreous

powder comprising essentially metallic copper particles having protective cuprous oxide films thereon and a substantial proportion of cuprous oxide, said cupreous powder being present in an amount substantially less than the amount of the dry mixture of magnesia and aggregate.

3. The manufacture of a cementitious material as claimed in Claim 1 or in Claim 2, wherein precipitated copper sludge is simultaneously dried and pulverized by means of a mill through which there is circulated a hot gaseous medium, until the water is substantially removed and the particle size is reduced to a few microns, e.g. two.

4. The manufacture of a cementitious material as claimed in Claim 1 or in Claim 2, wherein the water content of precipitated-copper sludge is reduced as rapidly as possible to approximately 10 per cent., the sludge being then transferred immediately to a mill where it is simultaneously dried and ground or pulverized, so that its water-content is further reduced to from 0.2 to 0.4 per cent., and it is ground or pulverised until its particle size is reduced to a few microns, e.g. two.

5. The manufacture of a cementitious material as claimed in Claim 4, wherein a hot gaseous medium is circulated through the grinding or pulverizing mill.

6. The manufacture of a cementitious material as claimed in any of Claims 3, 4 and 5, wherein the precipitated sludge, before transfer from the place of precipitation to the apparatus whereby it is dried and ground or pulverized, has its water-content brought to a value of at least 22 per cent. in order that the interstices between the particles shall be filled with water.

Dated this 20th day of September, 1948.

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